PART ONE
THE STRUCTURE OF LEUCENOL

PART TWO
A POLYMER OF α-ACETAMIDOACRYLIC ACID

BY

JAMES LESLIE JOHNSON

B.S., University of North Carolina, 1943

AN ABSTRACT OF A THESIS

SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS
FOR THE DEGREE OF DOCTOR OF PHILOSOPHY IN CHEMISTRY
IN THE GRADUATE COLLEGE OF THE
UNIVERSITY OF ILLINOIS, 1949

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LEIDEN

PART ONE

THE STRUCTURE OF LEUCENOL

Introduction

Degradation studies have shown leucenol from *Leucaena glauca Bentham* to be 1-(β-amino-β-carboxyethyl)-3-hydroxy-4-pyridone (1,2,3,4,5,6,7). The natural product was reported to be optically inactive by some workers (1,2) while others gave rotations of −9° (4), and −21° (6) or −22° (7).

It has been the purpose of this investigation to confirm the structure of leucenol by synthesis.

Discussion Of Results

4-Pyridone was found to add to acrylonitrile to yield 1-β-cyanoethyl-4-pyridone. α-Acetamidoacrylic acid and 4-pyridone reacted in a similar manner, and on hydrolysis of the condensation product α-amino-β-(N-4-pyridone)-propionic acid was obtained.

This last reaction provided a possible route to the synthesis of the leucenol molecule through the use of 3-methoxy-4-pyridone and α-acetamidoacrylic acid. The condensation was effected by heating the two reactants together in dioxane solution, without a catalyst, at 90-100°. The primary condensation product was hydrolyzed with aqueous hydriodic acid to yield *dl*-leucenol. When *dl*-leucenol crystallized from a boiling aqueous solution as the water was evaporated to a volume below that of saturation of the compound it was obtained in an anhydrous form. On the other hand, when a cold aqueous solution was permitted to evaporate the product was hydrated with one-half molecule of water. Natural leucenol did not form a hydrate under the same conditions. The infrared absorption spectra of the anhydrous and hydrated forms of *dl*-leucenol were different, and that of the anhydrous material resembled closely, but was not identical with that of natural

leucenol.

Although there seemed to be little doubt as to the identity of the synthetic product as *dl*-leucenol, a rigorous proof was desirable. On boiling in water for forty-eight hours natural leucenol was found to be racemized completely. The *dl*-leucenol thus obtained could be prepared in an anhydrous form or as a hemihydrate. The infrared spectra of these products were identical with those of the corresponding forms of the synthetic product. These results prove the structure assigned to leucenol to be correct.

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PART TWO

A POLYMER OF α-ACETAMIDOACRYLIC ACID

Introduction

A new type of polymer has been prepared from α-acetamidoacrylic acid. The first sample was obtained unexpectedly as the product from an attempted addition of

ammonia to the double bond of α-acetamidoacrylic acid in the presence of a catalytic amount of ascaridole. The purpose of this investigation was to initiate the characterization of the polymer.

Discussion Of Results

α-Acetamidoacrylic acid (1) polymerizes when a solution of the acid in aqueous ammonia is heated in the presence of a small amount of ascaridole. Viscosity determinations indicate the polymer, I, to be of moderately high molecular weight. The infrared spectrum of I shows a carboxyl group absorption at 1718 $cm.^{-1}$, and monosubstituted amide group absorptions at 1660 $cm.^{-1}$ and 1525 $cm.^{-1}$. The polymer, therefore, seems to be of the vinyl type.

Hydrolysis of I with aqueous hydrochloric acid resulted in a product, II, the structure of which has not been worked out. It contains nitrogen, but gave only a very faint blue color with ninhydrin, and a Van Slyke amino-nitrogen determination gave only a trace of nitrogen. Its infrared spectrum shows carboxyl group absorption at 1708 $cm.^{-1}$, but does not afford further indication as to the structure of the material.

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VITA

The author was born in Kipling, North Carolina, on February 13, 1921. He attended the public schools of Buies Creek, North Carolina, and was graduated from the Campbell High School in 1937. He attended Campbell Junior College from September 1938 to June 1940. The following September he entered the University of North Carolina, where he received the degree of Bachelor of Science in Chemistry in June 1943. He was employed by the American Cyanamid Company as an infrared spectroscopist from June 1943 to February 1946. He entered the Graduate College of the University of Illinois in March 1946. He held teaching assistantships until June 1947. He became a University Fellow in 1948.

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